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(54) Hot melt impulse ink jet ink.

(57) A hot melt ink jet ink comprises a dispersed solid pigment which is formulated in a wax, or high molecular weight fatty acid or alcohol vehicle to form a hot melt ink which is solid at room temperature but liquid at above 80°C, that is under the usual conditions of use. In a preferred embodiment, dispersed graphite in a non-evaporative oil carrier, such as mineral oil, is formulated with candelilla wax, stearic acid and/or behenic acid.

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BACKGROUND OF THE INVENTION

The present invention relates to the field of hot melt ink jet inks for use with impulse ink jet (drop on demand) type printers. More particularly, the present application relates to such ink jet inks which utilize solid pigments rather than soluble dyes as their colorants.

Originally, printing with hot melt type ink was suggested in connection with electrostatic printing apparatuses. In U.S. Patent No. 3,653,932 (Berry et al), entitled "Electrostatic Printing Composition Comprising Didodecyl Sebacate", an electrostatic printing process is disclosed using an ink comprised of one or more specified di-esters. In the Berry process, ink is heated into a fluid phase and is caused to form a convex meniscus at the nozzle tip by hydrostatic pressure. This pressure causes the end of the ink to intrude into an electrostatic field. Ink is then electrostatically drawn into a single field stream of droplets which traverses the span between the tip of the nozzle and the carrier. The preferred inks for use in this process are di-esters of sebacic acid which have been esterified with alcohols of paraffins having 12 or less carbon atoms in their chains. Each of the preferred inks is disclosed as having a melting point "which does not exceed about 51°C and a freezing point which is not below 30°C, to ensure that the ink will be in a liquid phase at the operating temperature at the exemplary reservoir, namely, about $56^{\circ} \pm 3^{\circ}\text{C}$, and that it "will be solid at generally encountered room temperatures to minimize its flow from the carrier. Berry et al discloses that such di-esters "provide excellent vehicles for pigments and dyes for producing

high quality electrostatic printing", and further discloses a number of examples using methyl violet toner, C.I. solvent yellow, C.I. solvent black. The methyl violet toner of the examples comprises about 40% methyl violet tanate in a transparent yellow mineral oil carrier.

U.S. Patent No. 3,715,219 (Kurz et al) discloses a similar electrostatic printing process using an ink composition comprising about 3% of a dye such as C.I. solvent black or C.I. solvent yellow. The remainder of the Kurz et al ink is a vehicle comprised of at least one alcohol of the paraffin series which has the general formulas $\text{CH}_3(\text{CH}_2)_n\text{CH}_2\text{OH}$, in which n is an integer between 12 and 26. According to Kurz, the preferred hot melt type inks have melting points which do not exceed about 61°C and freezing points which are not below about 30°C . During the process, ink in a fluid phase is supplied at a constant flow rate from a source represented by a supply tube to a reservoir which terminates at a nozzle with a capillary bore. The chamber of the exemplary apparatus is maintained at a temperature in the range of about 62°C and 82°C during the disclosed process. Viscosity of the disclosed inks is said to be within a range having an upper limit of 50 centipoises at operating temperatures, the exemplary inks in the Kurz et al references having viscosities of between 4.0-5.9 at 80°C .

More recently, impulse ink jet printing processes using hot melt inks have been disclosed. Impulse ink jet printing differs from electrostatic printing in that individual droplets are discharged from a printing head in response to relatively low pressures which are typically achieved using piezo-electric head elements. Unlike electrostatic printing

processes, such drop on demand processes produce much larger droplets which decelerate, not accelerate as they move toward the carrier.

One recent hot melt impulse ink jet ink is disclosed in U.S. Patent No. 4,390,369 (Merritt et al), entitled "Natural Wax-Containing Ink Jet Inks". This patent discloses the use of a number of natural waxes, such as Japan wax, candelilla wax, carnauba wax, etc. These waxes may be used at percentages of from 0.5 to 97.0% by weight either as the basic fluid vehicle of the ink or as an additive to other fluidic vehicles such as fatty acids, more particularly oleic or oleic acid with benzyl ether. Merritt et al disclose a number of such inks having viscosities of 6.7 to 15.7 at 165°F (about 74°C). Merritt et al disclose that a "coloring agent or a dye such as an oil or solvent soluble dye is usually added to the composition for visibility". The disclosed colorants include HD Victoria Blue, Calco nigrosine base, Acetosol Yellow, RLSN, and oil black BN.

A number of hot melt impulse ink jet inks other than the present ink have been developed at the present assignee's facility which are solid or semi-solid at ambient temperature. One preferred other ink is comprising stearic acid in an approximate weight range of 50-99%. Commercially available stearic acids are produced from saponified and distilled animal fats usually being composed of 60% liquid and 40% solid acid, the bulk of the liquid acids being separated from the solid acids by hydraulic pressing to produce for example, single pressed, double-pressed, triple-pressed stearic acids, etc. According to the Handbook of Chemistry and Physics (49th Edition), chemically pure stearic acid is octadecanoic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$)

(melting point 70.1°C). In addition to stearic acid, additives such as oleic acids, Typophor black, nigrosine base, benzyl ether, compounded or chemically modified waxes (including natural or other synthetic substances), a coloring agent or dye, such as oil or solvent soluble dye, etc. may be used to formulate hot melt inks.

Also, hot melt impulse ink jet inks have been developed by the present assignee comprising acid or alcohol vehicles in the C₂₀-C₂₄ range, significant proportions of a relatively high melting point ketone, such as stearone; a solid plasticizer, such as an acrylic resin; and a coloring agent, such as a dye. Alternatively, the vehicle may comprise waxes, such as candelilla wax and/or other specified waxes which melt above 65°C.

Numerous prior art references disclose a wide variety of colorants for use in other (non-impulse) printing or writing applications. For example, U.S. Patent No. 4,238,807 (Bovio et al) discloses a non-impact printing device which selectively emits solid ink particles from a rod of solid ink which is pulsed with high voltages to cause ink particles to be eroded from the rod and ejected through a nozzle on the paper. The rod of said ink is disclosed as consisting of carbon black compressed with 5 to 20% of stearic acid as a binder. In U.S. Patent No. 4,273,847 (Lennon et al) inks are disclosed for use in pulsed electrical printing. According to this process, ink particles, such as carbon particles are charged by conduction of current from other particles closer to a supporting sheet, detached by the electric

field and then caused to transfer to the receiving paper by the force induced solely by the electrical field.

Other inks containing pigment, such as carbon black are known for other purposes. U.S. Patents 3,421,910 (Gilson et al) and 3,330,673 (Voet et al) relate to a stencil paste and news printing inks, respectively, which use a dispersion of carbon black in mineral oil. U.S. Patents 4,337,183 (Santiago), 4,248,746 (Greiner) and 3,353,974 (Trimble) each disclose ink for purposes other than jet printers which use a carbon pigment in a vehicle. Patents including disclosures of glycerol, ethylene glycol, diethylene glycol and the like, with colorant materials such as pigments or dyes (most of which inks are water based) are disclosed in U.S. patents 3,421,910 (Gilson); 3,846,141 (Ostergren et al); 4,396,429 (Matsumoto et al); 4,395,287 (Kobayashi et al); 4,409,040 (Tobayashi et al); 4,421,559 (Owatari) and 4,176,361 (Kawada et al). U.S. Patent 4,443,820 discloses an ink which is solid at room temperature and liquid at an elevated temperature which contains more than ten percent of a dye dispersed in a hydrocarbon of the thermally dissoluble type. The ink is deposited on a (hctographic) master by discharging from a jet generating unit. The deposited ink is cooled hence forming an image configuration of solidified ink suitable for use in hectographic printing of a number of reproductions of an original image. The ink in its liquid form has a viscosity of 3 to 20 c.p.

Notwithstanding the above-mentioned disclosures, a need exists to provide improved impulse ink jet inks which are capable of producing copy which approaches or exceeds the copy of standard impact-type

printing, such as that which may be produced from a standard office typewriter or daisy-wheel printer. Such an ink should be readily jettable, easily stored and shipped for extended periods of time without separation or degradation yet be capable of providing a sharp, dark, well defined copy when placed into use.

SUMMARY OF THE INVENTION

The present invention provides a novel, hot melt ink jet ink containing a solid pigment dispersed in a vehicle comprising a C₁₈-C₂₄ acid or alcohol; or a wax having a melting point above 65°C. The preferred ink is solid at room temperature, but has a jettable viscosity when heated to temperatures above the melting point of the vehicle, preferably above 80°C. The preferred ink further comprises an oil carrier in which the solid pigment is originally dispersed, which carrier is compatible with the acid, alcohol or wax vehicle. Unlike lower molecular weight vehicles, such as oleic acid vehicles, the graphite pigment will not settle out or separate even after extended times in the liquid state.

Accordingly, a non-evaporative ink system is provided for ink jet printing which is light fast, exhibits excellent archival properties, little or no corrosion, good edge definition, good thermal stability, and good dot size. The subject inks exhibit little or no lateral spread when the drop hits the paper, provides potential for laminatable prints, and offers the possibility of providing bright colors, true process color printing and OCR readable copy.

The preferred ink of the present invention utilizes a pre-dispersed suspension of colloidal graphite having particle sizes of less than one micron,

which are easily jetted through a 50 to 75 micron ink jet nozzles. Although the graphite particles would tend to settle out of inks having liquid vehicles, the high molecular weight, compatible nature of the disclosed inks prevents such separation even during extended operation at jetting temperatures.

The present invention also provides a method of ink jet printing which comprises (a) heating an ink of the invention to at least 80°C; (b) discharging droplets of said ink at said temperature towards a print substrate; and (c) allowing the ink to solidify on impact to form print on the substrate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides a novel hot melt ink jet ink composition for use in an impulse ink jet apparatus comprising a solid pigment dispersed in a vehicle comprising a C₁₈-C₂₄ acid or alcohol, or even more preferably, wax having a melting point above 65°C.

As used herein, the term "pigment" refers to visible materials which are not soluble, but are suspended or dispersed as fine particles in the subject ink. The preferred solid pigment is a colloidal graphite having a particle size less than 25, preferably less than 10, more preferably less than one micron, which is carried in a non-evaporative oil carrier, such as mineral oil. Graphite is particularly preferred as a pigment when black is the desired color, however, other known pigments such as carbon black and barium lithol, are suitable for use in the present invention provided they meet aforementioned particle size requirements and do not unacceptably agglomerate or settle from the subject ink.

As mentioned above, one preferred vehicle is a C₁₈-C₂₄ fatty acid vehicle, or alcohol, acids being preferred over alcohols. Stearic acid or behenic acids are two such suitable acids, behenic presently being preferred over stearic. The preferred embodiment vehicle is a wax, particularly candelilla wax, having a melting point above 65°C. Other waxes believed suitable include bamboo leaf, certain bees waxes, caranda, carnauba, hydrogenated castor oil, Chinese insect, cotton, cranberry, certain Douglas-fir bark, asparto, certain flax, Indian corn, Madagascar, most micro-crystalline waxes, montan, ouricury, ozocerite, palm, peat wax, rice bran, shellac wax, sisal hemp, sorghum grain, Spanish moss, refined sugar cane waxes and mixtures thereof, each of which waxes has a melting temperature above about 65°C. Mixtures of such waxes found suitable for jetting include a 50-50 mixture of candelilla and carnauba (97% wax, 3% dag).

In the preferred embodiment the solid pigment should comprise 0.1-10 wt%, preferably 1-5 wt%, more preferably 2-3 wt% of the ink. The herein disclosed vehicle of the subject ink should normally comprise 50-99.1, preferably 90-99 wt%, more preferably 95-98 wt% of the subject ink. The subject ink jet ink should normally have a maximum viscosity of about 15 centipoises, preferably less than about 14 centipoises, when discharged from an impulse ink jet apparatus at elevated temperatures, preferably above about 80°C.

In addition to the above-described components, the ink of the present invention may comprise additional additives, including ketones preferably of m.pt in the range 65 to 120°C, such as stearone or laurone, which ketones should preferably not exceed 50 wt % of said ink. The disclosed inks may optionally also contain up to 4 wt % of a plasticizer, such as an acrylic resin plasticizer. For a further description of such additives reference is made to co-pending European Patent Application 85.305977.2, which is incorporated by reference herein.

In addition to providing a novel ink, the present invention provides a novel method of hot melt impulse ink jet printing comprising the steps of (a) providing a hot melt impulse ink jet ink comprising at least a solid pigment dispersed in a vehicle comprising C₁₈-C₂₄ fatty acids or alcohols; or wax(es) having melting point(s) above 65°C; (b) heating said impulse ink jet ink to a temperature above 65°C, preferably above 80°C to obtain a composition having a viscosity below about 15 centipoises, and (c) impulse jetting said ink jet composition at said elevated temperature against a substrate whereby said composition solidifies to form hot melt print.

The use of solid pigment, such as colloidal dispersed graphite overcomes many of the difficulties which are encountered in using dyes in such inks. At high temperatures, such as the temperatures preferred for jetting hot melt inks, dyes are not as stable as pigments, not as strong in color, nor as permanent. The chief advantage of dyes are that they are soluble in most ink formulations and will not settle or separate during the storage shipment or use of such inks.

Applicants have recognized that when high molecular weight, relatively high melting point vehicles, such as C₁₈-C₂₄ fatty acids or waxes are utilized, colloidal graphite will be frozen in suspension during non-operating periods. Furthermore, it has been found that, even when heated, high melting point materials, such as candelilla wax, maintain the suspension of such graphite particles for much longer times than corresponding liquid inks, such as oleic acid based inks. Furthermore, thermal stability and other advantages of such pigments would be highly advantageous, even if agitation were to be used to maintain their colloidal suspension over extended periods of time.

The present invention may further be understood from the following examples:

EXAMPLE 1

Oil Dag (dispersed Acheson graphite) in mineral oil was diluted to approximately 2% solids (graphite) with oleic acid, with a resultant viscosity of about 60 cps at 20°C and 13 cps at 57°C. This ink comprised 95 wt% oleic acid, 3 wt% mineral oil and 2

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wt% graphite. This solution was jetted using a standard liquid impulse ink jet system, available under the tradename "Archer Imaging Subsystem". Character printing was conducted yielding high quality, highly defined dots and characters. The system was operated for at least 4 hours, allowed to stand overnight, and refired acceptably the next day. No adverse effect of particulate matter influencing the performance was noticed, however the subject pigment had tended to settle, and, over two days the subject ink gradually lost its color and became colorless. This ink would be unsuitable for use in impulse ink jet printing because, during storage, shipment and/or normal use the dispersed graphite would settle to the point where its resuspension for jetting would not be practical.

EXAMPLE 2

An impulse ink jet ink was prepared comprising .95 wt% candelilla wax and 5 wt% oil dag, again to provide an ink having about 2 wt% colloidal graphite, and 3 wt% mineral oil. The resulting ink was found to have excellent jettability at an operating reservoir temperature of between 90-120°C. Its viscosity at 110°C was about 10 cps. The subject ink produced very good print quality, both initially, and after 199 hours of standing at operating temperature in the liquid state. It is believed that these results stem in part from the excellent compatibility between the subject vehicle and the colloidal graphite in the subject composition, and also possibly the effects of convective currents within the subject ink at the 90°C + operating temperatures of the subject test.

EXAMPLE 3

An impulse ink jet ink was prepared comprising 95 wt% stearic acid, 2 wt% colloidal graphite, and 3 wt% mineral oil. The resulting ink had a viscosity at 80°C of 10 cps. Stearic acid represents one of the lower molecular weight acids suitable for use as the vehicle for the herein disclosed inks, and is presently not as preferred as such higher molecular weight acids as behenic. Nonetheless, this stearic acid ink was found to exhibit suitable jettability and good print quality initially, and over a period of 16 hours (overnight) while left standing at operating temperatures of 90°C. While such a standing time is presently not believed to be acceptable for most commercial applications, the use of such a pigmented hot-melt ink impulse ink jet ink on a commercial basis may nonetheless be facilitated if incorporated with other known techniques for improving the stability of dispersions, including for example, the use of emulsifiers. It is further anticipated that the use of proportions of stearic acid with high melting point ketones, such as stearone or laurone, or with additions the aforementioned waxes or higher molecular weight fatty acids or alcohols might further improve the long term stability of such inks.

In view of the above, it is anticipated that materials such as the aforementioned fatty acids or alcohols of relatively high molecular weight and the aforementioned waxes which melt above 65°C are particularly suitable vehicles for use in formulating inks of the present invention.

CLAIMS:

1. A hot melt ink jet ink composition for use in an impulse ink jet apparatus, comprising a solid pigment dispersed in a vehicle comprising a wax having a melting point above 65°C, or a C₁₈-C₂₄ fatty acid or alcohol, said ink being solid at room temperature.
2. An ink as claimed in claim 1, wherein said solid pigment is dispersed in an oil carrier, preferably a mineral oil, compatible with said vehicle.
3. A hot melt ink as claimed in claim 1 or claim 2, wherein said solid pigment is colloidal graphite having a particle size of less than 25 microns.
4. A hot melt ink as claimed in any preceding claim, wherein said ink comprises 0.1-5 wt % of graphite.
5. A hot melt ink as claimed in any preceding claim, wherein said wax is candelilla wax.
6. A hot melt ink as claimed in any preceding claim, wherein said acid is stearic acid and/or behenic acid.
7. A hot melt ink as claimed in any preceding claim, wherein said ink includes a ketone having a melting point between 65-120°C.
8. A hot melt ink as claimed in claim 7, wherein said ketone is stearone.

9. A hot melt ink as claimed in any preceding claim and having a maximum viscosity of 14 centipoises at above 80°C.

10. A method of ink jet printing comprising:

(a) heating an ink defined in any preceding claim to at least 80°C;

(b) discharging droplets of said heated ink towards a print substrate; and

(c) allowing the ink to solidify upon impact with the substrate to form print thereon.

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